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No. 64329-4

EPITAXIAL GROWTH OF CdSnP_2 ON InP
FOR MICROWAVE FETs

6 October 1980

By

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CdSnP ₂ platelets were grown from Sn solutions to provide samples for characterizing ohmic and Schottky barrier contacts. High temperature Hall and resistivity measurements indicate that the observed n-type conductivity is due to a deficiency of the volatile constituents; probably phosphorus. Both liquid phase and molecular beam epitaxy were examined for the epitaxial growth of CdSnP ₂ on InP substrates. Best results were obtained with an open tube liquid phase system using a step-cooling technique.		

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~~20. Abstract (Continued)~~

X-ray diffraction measurements indicate a lattice mismatch
of about - 0.5% for these layers.



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EPITAXIAL GROWTH OF CdSnP_2 ON InP
FOR MICROWAVE DEVICES

1. RESEARCH OBJECTIVES

Because of their lower effective masses, different band structure, and good lattice match to their analog III-V compounds, some of the II-IV-V₂ compounds may be important for heterostructures and high-speed device applications. The objectives of the work reported here are to:

- (1) develop techniques for the growth of high-quality epitaxial CdSnP_2 on InP ;
- (2) minimize electrically-active defects and residual impurities in this material to achieve well-controlled doping;
- (3) investigate the electrical transport properties of CdSnP_2 to determine its suitability for heterostructures and high-speed device applications; and

(4) develop the technology required for the
fabrication of suitable device structures.

With these results we expect to gain substantial insight
into the potential of CdSnP_2 for electronic applications.

2. SOLUTION GROWTH OF CdSnP₂ PLATELETS

2.1 GROWTH PROCEDURE

CdSnP₂ was initially grown as platelets from a Sn solution to make material property measurements and for possible use as a source material in the LPE system. Following a procedure described by Buehler *et al* [1], elemental Cd, Sn and red P₄ were placed in a vitreous carbon boat and sealed in an eight inch 25 mm O.D. quartz ampoule evacuated to a residual pressure of 2×10^{-6} torr. All elemental material used were 99.999% pure. The quartz ampoule was nominally 1 mm thick to withstand the phosphorus pressures produced on heating. The carbon boat, quartz ampoule and quartz sealing plug had been cleaned in aqua regia for 24 hours and baked out under vacuum prior to loading. The ampoule was heated over a period of six hours, allowed to homogenize for one hour, and then slowly cooled to 230°C. A schematic of a typical sealed ampoule is shown in Figure 1. Data for these growth runs are given in Table 1.

The resulting ingots containing CdSnP₂ in Sn were immersed in Hg and heated to about 60°C to dissolve the Sn. The CdSnP₂ crystals were separated from the bulk of the Hg-Sn solution by passing it through a gauze sieve and the remaining solution was removed in 33% HNO₃. The resulting CdSnP₂ material was typically in the form of

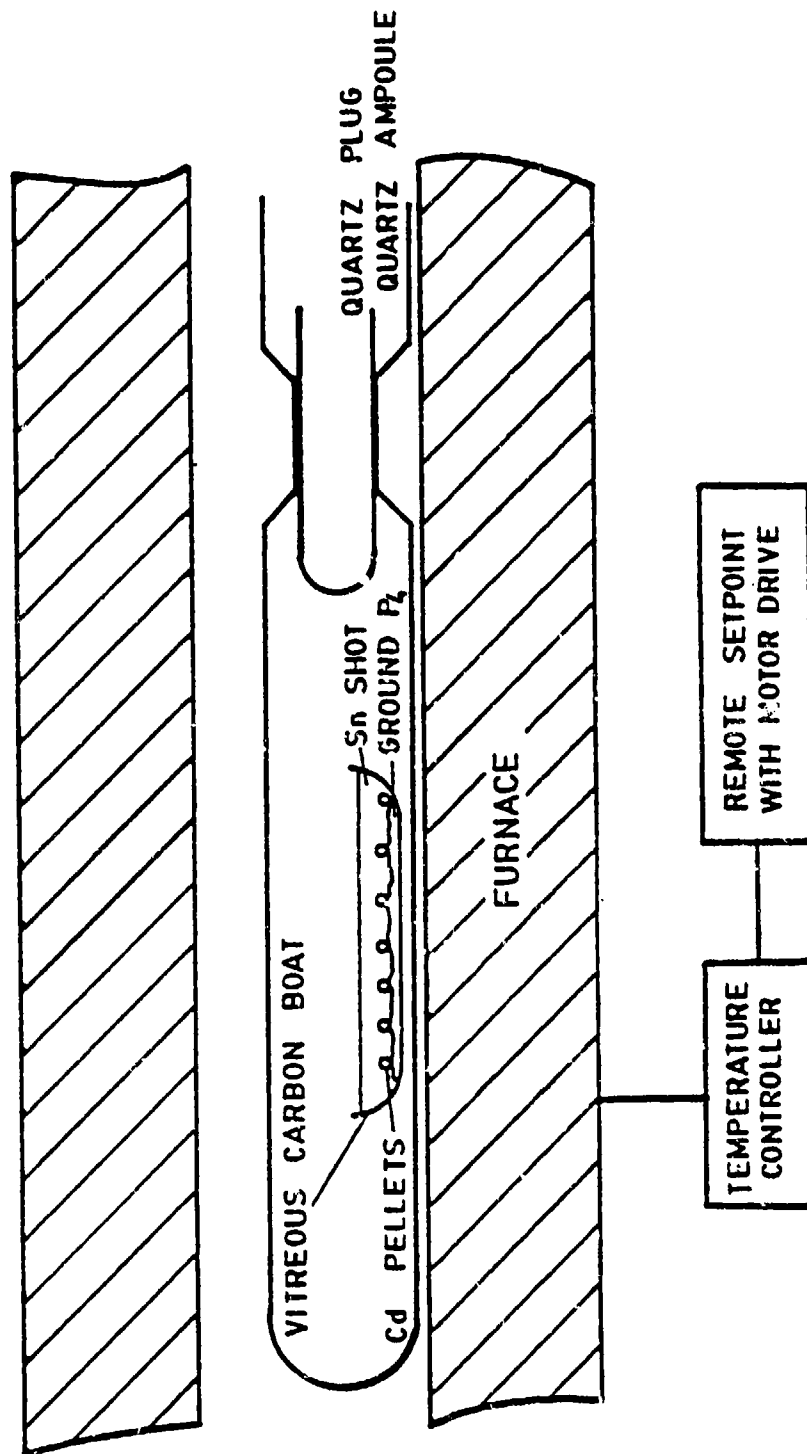


Figure 1 Sealed ampoule system used for growing CdSnP_2 platelets.

Table 1. Data for sealed tube CdSnP₂ platelet growth.

RUN	MOLAR % Cd	MOLAR % Sn	MOLAR % P	TOTAL MASS (Grams)	HOMOGENIZATION TEMPERATURE (°C)	COOLING RATE (°C/Hr)
C-5	1.8	94.7	3.5	23.1	600	2.5
E-1	2.5	92.5	5.0	10.4	600	2.5
E-3	8.0	76.8	15.2	11.2	700	10.0
E-4	10.9	69.2	19.9	9.8	715	10.0
E-5	8.0	74.0	18.0	10.1	600	10.0
E-6	8.0	77.0	15.0	11.3	600	10.0
E-7	5.8	83.6	10.6	13.3	700	7.3
F-1	8.0	76.8	15.2	11.2	850	2
F-2	7.9	77.0	15.0	11.3	700	5
F-3	8.0	76.9	15.1	11.2	700	5
F-4	7.0	79.0	14.0	11.0	700	5

10 mm x 4 mm x 3 mm odd shaped single crystals mixed with an abundance of smaller crystals (2 mm x 2 mm x 2 mm).

2.2 SAMPLE PREPARATION

Experimental samples were prepared from the larger platelets by chemical-mechanical polishing with a 1% Br in methyl alcohol solution. The resulting samples were 100 μ m to 400 μ m thick with parallel flat surfaces of area .25 cm^2 to .50 cm^2 .

2.3 CONTACTS

Ohmic contacts were made to the CdSnP_2 samples using 10 mil and 20 mil diameter Sn spheres alloyed at 300°C for two minutes in a high purity hydrogen atmosphere. These contacts were found to have a contact resistance of $1.9 \times 10^{-4} \Omega \text{ cm}^2$ at 300 K. Although these contacts adhered well to the sample surface at 300 K they tended to break off of the samples when immersed in liquid nitrogen. No contact resistance measurements were made at 77 K.

Gold plated onto the surface of several samples produced softly rectifying contacts. The contacts were alloyed for twenty seconds at 300°C in a hydrogen atmosphere to produce ohmic contacts. No contact resistance measurements were made on these contacts

Al contacts evaporated onto the surface of several samples gave rectifying contacts with various reverse breakdown voltages ranging from one to five volts.

The best barriers were obtained by evaporating Al onto the entire sample, masking contact regions with apiezon wax, and removing the excess Al in HF. The contacts produced in this manner had higher breakdown voltages than those produced by Al evaporation through a glass or metal mask.

2.4 HALL AND RESISTIVITY MEASUREMENTS

The majority of CdSnP_2 samples were used for Van der Pauw Hall measurements at 300 K, 77 K, and at elevated temperatures (300 K to 675 K). These samples were prepared as described above with four 10 mil diameter Sn contacts alloyed to the sample surfaces. Those samples which were measured at elevated temperatures were encapsulated with pyrolitic SiO_2 grown at 300°C. The encapsulant layers were .20 μm to .40 μm thick.

The samples measured at 300 K were n type with a mean carrier concentration of $1 \times 10^{17} \text{cm}^{-3}$ and a mean mobility of 725 $\text{cm}^2/\text{V sec}$. The better samples had carrier concentrations in the range of 5×10^{16} to $8 \times 10^{16} \text{cm}^{-3}$ with mobilities of 1400 to 2000 $\text{cm}^2/\text{V sec}$. When these samples were measured at 77 K no substantial change in the carrier concentrations or mobilities from the 300 K values were observed. 300 K and 77 K measurements were made using a 2.15 kG permanent magnet.

High temperature Hall measurements were made in the apparatus shown schematically in Figure 2. These measurements were made in hydrogen purified by a palladium diffusion cell using a flow rate of 15 ml/mm. A 3.5 kG magnetic field produced by a four inch electromagnet was used for these measurements.

High temperature measurements of the encapsulated samples were limited to temperatures below 700 K due to irreversible changes in the samples. The results of measurements on a typical sample are plotted in Figure 3. In these experiments the temperature was increased from room temperature and measurements were taken every 25 K. The circles in Figure 3 are the data for the initial set of measurements and the squares are from a subsequent set of measurements which were made after the sample had returned to room temperature. These data indicate a steady increase in the carrier concentration and decrease in the mobility with increasing temperature up to 600 K. Above 600 K the changes accelerate and are irreversible as can be seen from the lower mobilities and higher carrier concentrations at low temperatures in the latter measurements.

The irreversible changes are due to loss of volatile constituents from the samples; probably

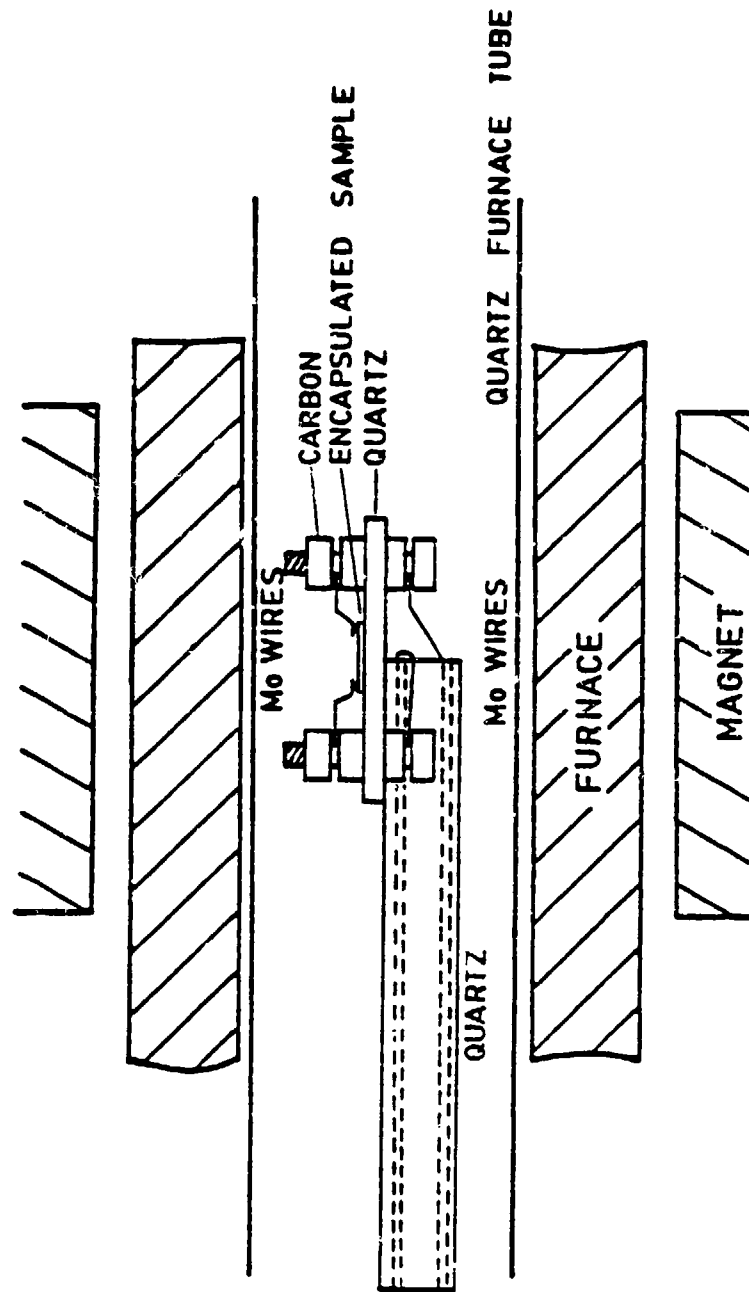


Figure 2 Schematic of high temperature Hall measurement apparatus.

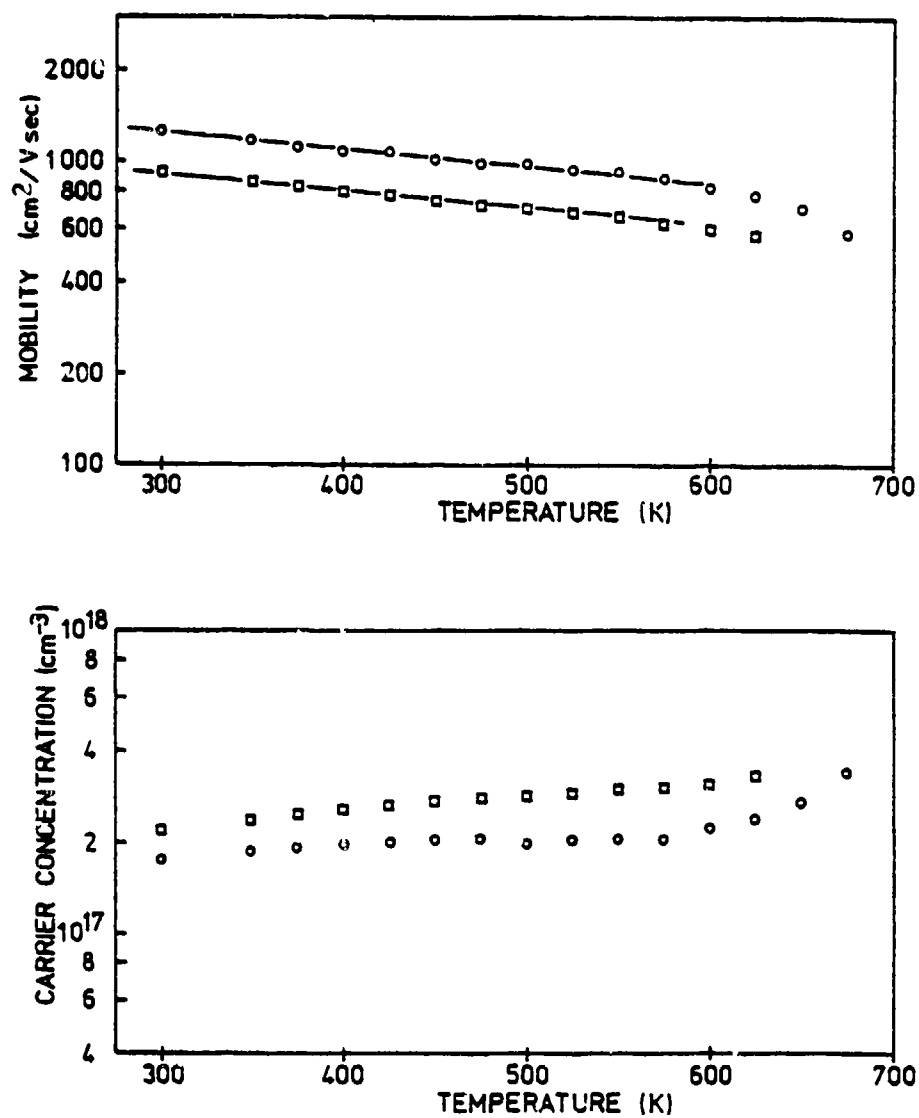


Figure 3 High temperature Hall data for a CdSnP_2 platelet sample.

phosphorus due to its high vapor pressure. This is supported by the observation of numerous cracks in the encapsulating layers of the samples after measurements were made. The above data indicate that depletion of volatile components from the samples causes an increased n type carrier concentration and a decreased mobility. Thus, to produce epitaxial layers of high quality emphasis should be placed on maintaining a high concentration of the volatile component in the growth melts.

3. LIQUID PHASE EPITAXIAL GROWTH OF CdSnP₂

3.1 SEALED TUBE EPITAXIAL GROWTH

Epitaxial growth experiments were initially performed using a tipping boat arrangement described by Shay *et al* [2] which is shown schematically in Figure 4. In these experiments a carbon boat was used to contain the substrate and growth melt. The growth melt was homogenized in a separate step by loading the cleaned carbon boat with 99.999% Cd, Sn, and red P₄ and sealing the boat in a cleaned quartz ampoule evacuated to a residual pressure of 2×10^{-6} torr. The starting materials were measured to give a molar composition of 94% Sn, 2% Cd, and 4% P with a total mass of 10.6 grams. This ampoule was then heated to 600°C over a period of six hours, allowed to homogenize for an hour, and quenched. The quartz ampoule was broken open, a substrate was inserted into the carbon boat, and the boat was sealed in another quartz ampoule after evacuating to 2×10^{-6} torr and backfilling with argon to 620 torr. The {100} Fe-doped InP substrate had been prepared by chemical-mechanical polishing one face with 4% bromine-methyl alcohol followed by cleaning in boiling trichloroethylene, acetone, and methyl alcohol, and a four minute etch in 2% bromine-methyl alcohol. The loaded ampoule was held in a verticle furnace as shown in Figure 4 and was rapidly heated to 525°C and allowed

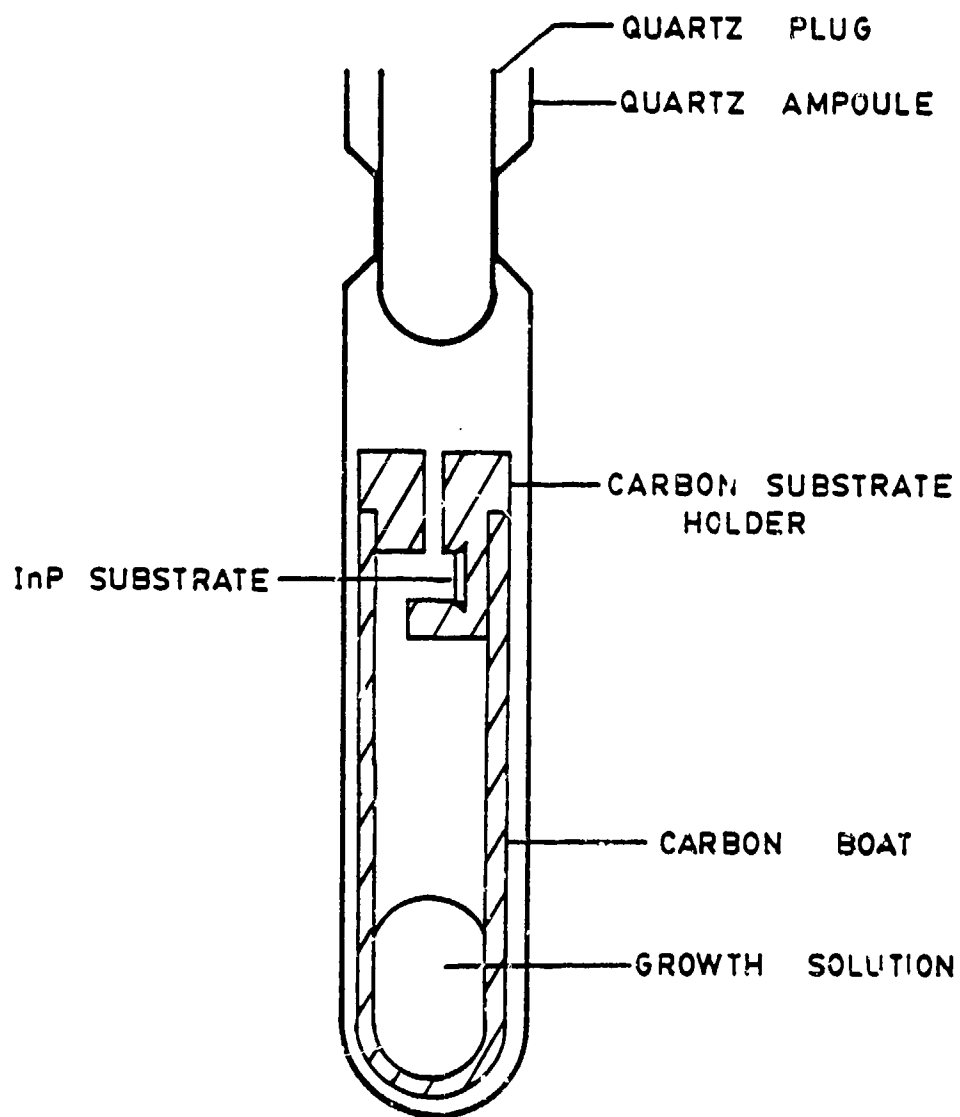


Figure 4 Schematic of sealed tube tipping LPE system.

to equilibrate for fifteen minutes. The furnace was then cooled to 510°C and rotated 180° so that the melt solution would flow over the substrate and out of the hole in the substrate holder as the furnace was cooled 10°C/hour. When the furnace had cooled to 360°C it was tipped back to its original position and the ampoule was quenched. The separate homogenizing run, argon backfill, and the baffle on the substrate holder were all used to decrease the transport of volatile constituents from the melt to the substrate before melt contact was made. These constituents were found to cause severe pitting of the substrate.

The epitaxial growth produced in this manner was very rough with uneven interfaces. A typical cross section of a sample is shown in Figure 5. The epitaxial layers were generally 100 μ m thick. No Hall measurements were made on these layers.

Because of the poor layer quality little time was spent working with this system. Instead, an open tube H₂ flow system was designed and constructed for epitaxial growth. Such a system has several advantages over the closed tube system in that the apparatus and materials can be additionally purified, an *in situ* etch can be used, less materials are used in each growth run, and the growth runs are more easy to control over shorter times.



Figure 5 Cross section cleave of sealed tube LPE sample after chemical-mechanical polishing with 1% bromine-methyl alcohol.

3.2 OPEN TUBE FLOW SYSTEM

The open tube LPE system shown schematically in Figure 6 was designed and constructed. This system consists of a high purity graphite sliding boat with stationary melt wells and a slider with 0.015" deep substrate wells. This boat sat in a 40 mm O.D. quartz furnace tube through which purified hydrogen flowed. In between growth runs the system was baked out for four hours at 600°C with a flow rate of 120 ml/min.

The {100} InP substrates used in these experiments were chemically-mechanically polished on one side and their backs were lapped using 5 μm and 2 μm grit to a thickness of 400 μm . These substrates were then cleaned and etched as described above. The final chemical etch removed approximately 30 μm of material from the surface. The {111} and {211} InP substrates were prepared by lapping both faces to produce substrates 400 μm thick with parallel flat faces followed by cleaning in boiling organic solvents and a chemical etch for two minutes in 1% bromine-methyl alcohol. Substrates prepared in this manner would fill the substrate wells so that most or all of the growth solution could be removed after growth. All substrates used in these experiments were Fe-doped semi-insulating InP.

The LPE boat was loaded by placing the substrates in the substrate wells, positioning them between the

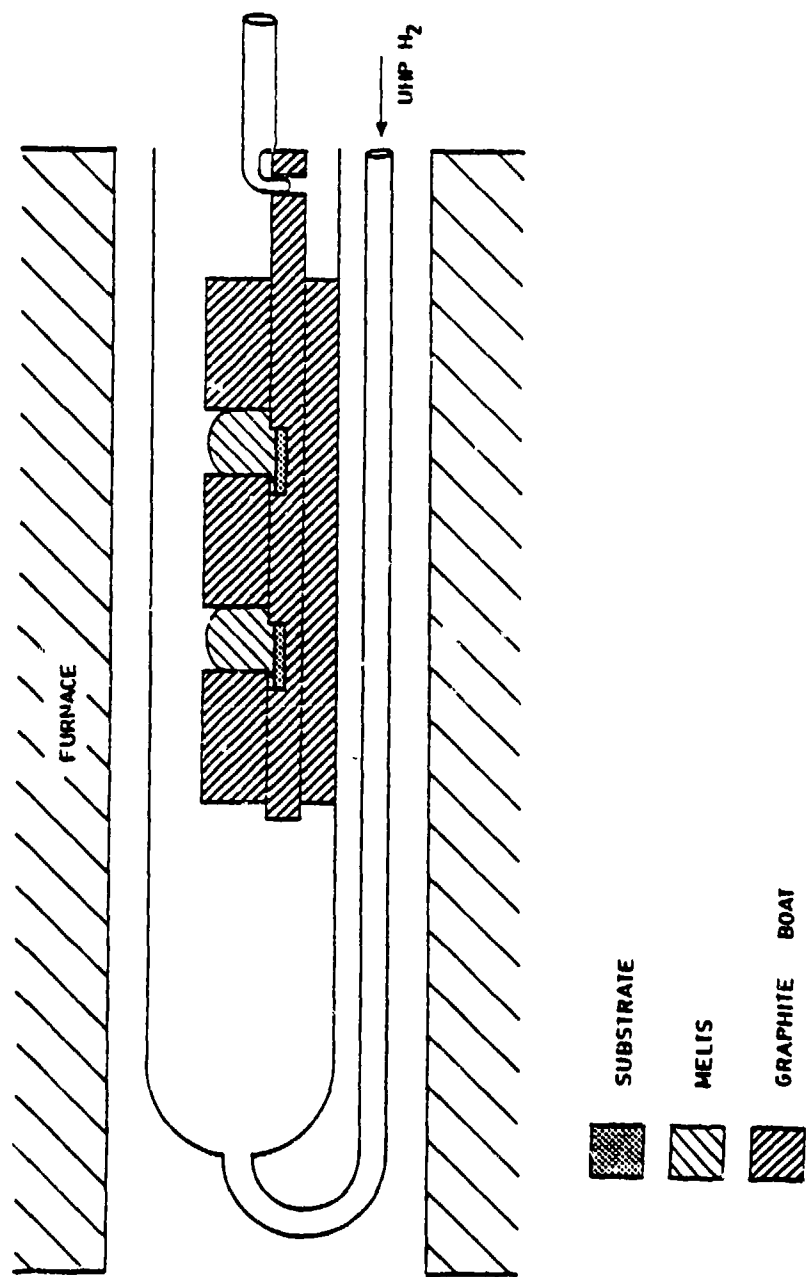


Figure 6 LPE sliding boat system.

melt wells, and then loading the melt wells with growth materials or etch materials. The boat was then loaded into the furnace tube and rapidly heated to the homogenization temperature. The melt was allowed to homogenize for one to two and a half hours and then cooled to the growth temperature: typically 20°C below the homogenization temperature. At this point the substrate was etched and moved to contact the growth solution. The furnace was then cooled at a constant rate: generally 5°C/hr or 10°C/hr . A twenty second etch of the substrate in pure Sn removed the top 5 μm of the surface and gave a much better surface for epitaxial growth than an unetched substrate. Such an etch was used in all of the growth runs except for the initial few.

3.2.1 Cd-P₄-Sn System

In the first forty three growth runs the growth melt was made up of 99.999% purity ground red P₄, pellet Cd, and Sn shot with molar composition 15% P, 7% Cd, and 78% Sn. The homogenization temperature used was 540°C and the initial growth temperature varied between 490°C to 525°C . Followed by a 10°C/hr cooling rate for four to ten hours. This procedure was discontinued because of the inability to consistently saturate the solution at a given temperature. This was due to loss of material from the melts before

the melts could be homogenized and during growth. Epitaxial material was grown in this system but this material was in the form of isolated single crystals and rough epitaxial layers. The best CdSnP_2 layer grown in this system is shown in Figure 7.

3.2.2 Cd_3P_2 -Sn System

To better control the CdSnP_2 concentration in the melts so that the saturation temperature could be more accurately controlled, two changes in the procedure were made. First, a Cd_3P_2 source material was used in place of Cd and P_4 to allow for more complete dissolution of the source materials in the Sn solution. Second, the composition of Cd and P in the melt was reduced to lower the homogenization and initial growth temperatures and reduce the loss of volatile constituents from the melt.

The Cd_3P_2 source material was grown in a sealed tube system shown schematically in Figure 8. In this system a 25 mm O.D. 20 inch quartz ampoule was loaded with a boat of Cd pellets at one end, red P_4 at the other end, and sealed at a residual pressure of 3×10^{-6} torr. Stoichiometric amounts of Cd and P_4 were used with a slight amount of excess P_4 to provide a phosphorus overpressure in the ampoule. A total mass of 30 grams of the constituents was used per growth run. This ampoule was placed in a furnace and



Figure 7 Cross section cleave of CdSnP_2
epitaxial growth from a solution
of P_4 and Cd in Sn on {100} InP.

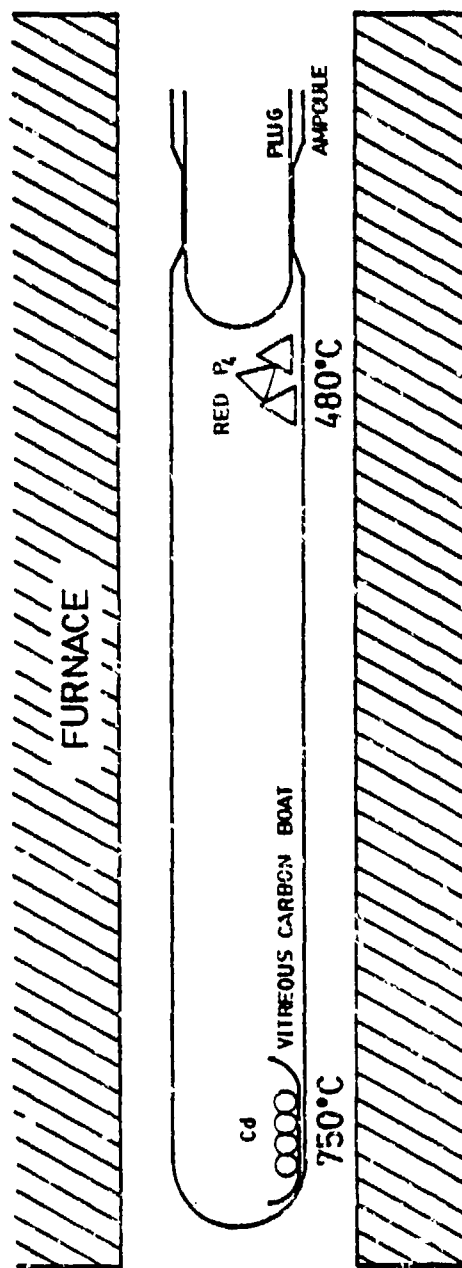


Figure 8 Schematic of sealed tube method for the growth of Cd_3P_2 .

heated over eight hours with the cadmium at 750°C and the phosphorus at a mean temperature of 480°C . This cadmium temperature was chosen to be slightly above the melting point of Cd_3P_2 and the phosphorus temperature was used to give a phosphorus pressure of approximately two atmospheres in the ampoule. The ampoule was allowed to homogenize for 100 hours and was then cooled to room temperature. Cd_3P_2 growth was observed near the center of the ampoule in a region where the temperature had averaged 630°C . All of the cadmium and phosphorus had been consumed. Some of the Cd_3P_2 was in polycrystalline form adhering to the walls of the ampoule with large single crystals growing toward the center of the ampoule. These larger crystals were used for the source material.

Liquid phase epitaxial growth has resumed using a melt solution of molar composition 1.5% Cd_3P_2 and 98.5% Sn. The homogenization temperature was decreased to the 430°C to 455°C range with a two and a half hour homogenization time and the initial growth temperature was typically 420°C . Both $5^{\circ}\text{C}/\text{hour}$ and $10^{\circ}\text{C}/\text{hour}$ cooling rates were used with little effect on the growth. $\{100\}$, $\{111\}$, and $\{211\}$ substrate surfaces were used and no preference for any orientation was observed. In these experiments the saturation temperatures were more stable although there were still some fluctuations.

At temperatures above 455°C excessive Cd and P loss from the melts was observed.

The layers grown in this manner again tended to have rough surfaces and dendritic growth. A typical layer is shown in Figure 9. Hall measurements on this material indicated that it was n type with a carrier concentration of $1 \times 10^{18} \text{ cm}^{-3}$ and a mobility of $200 \text{ cm}^2/\text{V sec}$. The high temperature Hall measurements indicate that the poor material quality is due to depletion of volatile constituents from the melt.

X-ray diffraction measurements were made on some of the epitaxial layers and some of the data are plotted in Figures 10 and 11. The measurements indicated a mismatch of -0.4% to -0.6% as compared to calculated mismatches of -1.9% or +0.5% based on the lattice parameter measurements of Shay *et al* [2]. The differences in measured and calculated values are probably due to differences in the growth techniques. The peak at -1.8% mismatch in Figure 11 is due to polycrystalline regions in that sample.

3.2.3 Step Cooling Technique

In the most recent LPE growth experiments a step cooling technique was used. In this technique the melt is cooled a few degrees below the saturation temperature before contacting the substrate and growth is carried out at a constant temperature. This was performed



Figure 9 Cross section cleave of CdSnP_2
epitaxial growth from a solution
of Cd_3P_2 in Sn on $\{211\}$ InP In face.

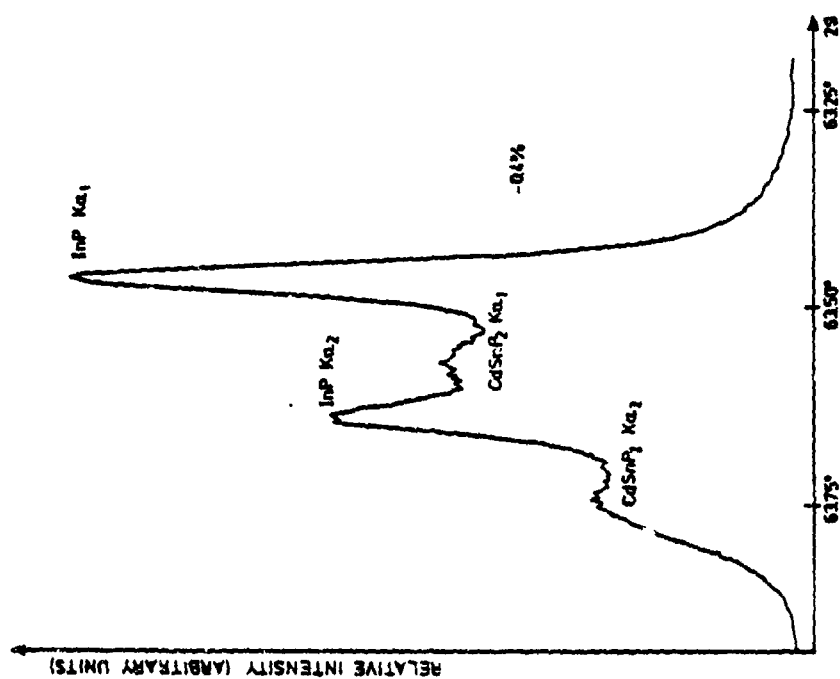


Figure 10 X-ray diffraction measurements for
 CdSnP_2 in $\{100\}$ InP.

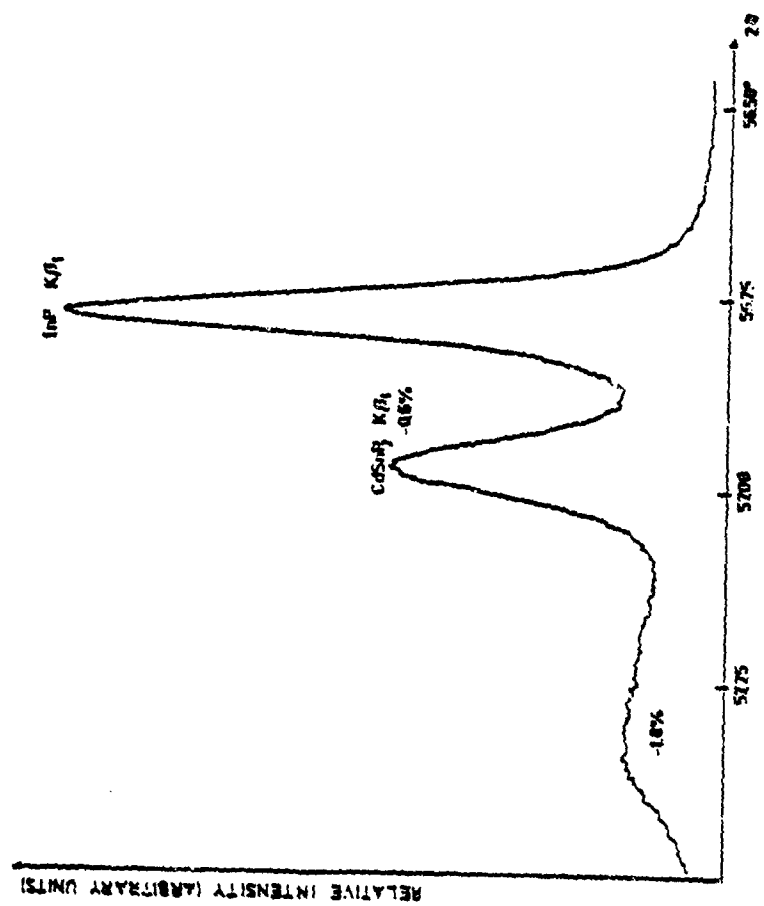


Figure 11 X-ray diffraction measurements for CdSnP_2 in (100) InP.

using a source solution of 1.5% Cd_3P_4 and 98.5% Sn homogenized at 430°C for two and a half hours and cooled to 415°C before contacting the substrate. This technique produced the best surface morphology observed so far. A layer grown using this technique is shown in Figure 12. This technique appears to be the most promising for uniform thin layer growth and a new boat is being constructed for further step cooling experiments. No Hall data or X-ray diffraction data have as yet been obtained for these layers.

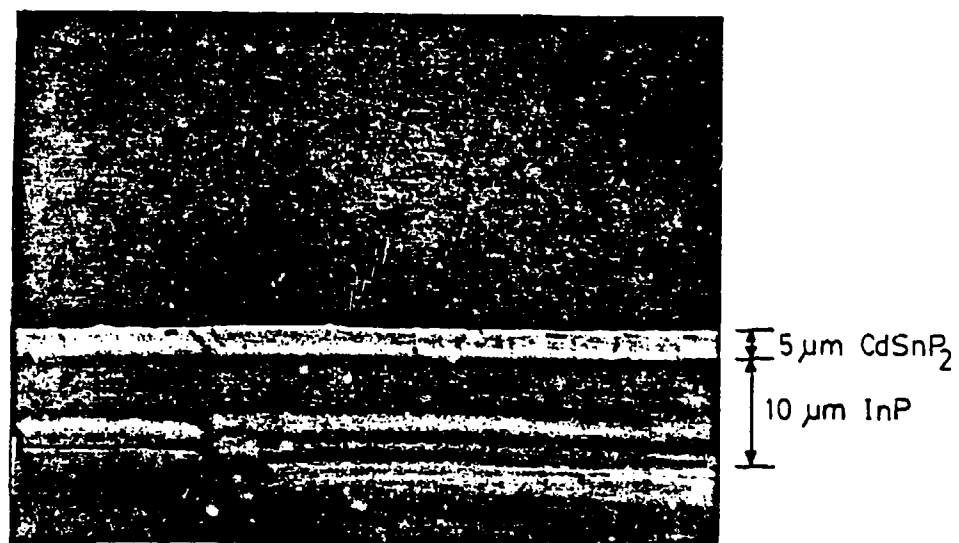


Figure 12 Cross section cleave of CdSnP₂ epitaxial layer grown using the step cooling technique on {100} InP.

4. MOLECULAR BEAM EPITAXIAL GROWTH OF CdSnP₂

4.1 GROWTH APPARATUS

Figure 13 shows the apparatus used to grow CdSnP₂ epitaxially on InP substrates. Three effusion cells are used: one for each of the constituent elements. The Cd and P cells are both maintained at low temperatures and are constructed completely of high-purity quartz with platinum heating elements. The Sn effusion cell in the center must be operated at high temperatures and consists of a pyrolytic carbon cell with a tantalum heating element. A tantalum heat shield with water cooling coils is used to surround the Sn cell to reduce heating of the adjacent parts of the vacuum system and maintain control of the lower temperature Cd and P cells.

The InP substrate heater is a Mo block with embedded heaters and control thermocouples. The substrate holder is a ladder arrangement with four Mo "rungs" separated by two stainless steel rods so that four epitaxial growth runs can be performed in each pump-down cycle. The ladder which holds the InP substrates is in tension against the Mo heater block to obtain good thermal contact. Between the substrates and the effusion cells is an electrically-activated shutter on a liquid-nitrogen-cooled shield. This arrangement has an important advantage: the growing

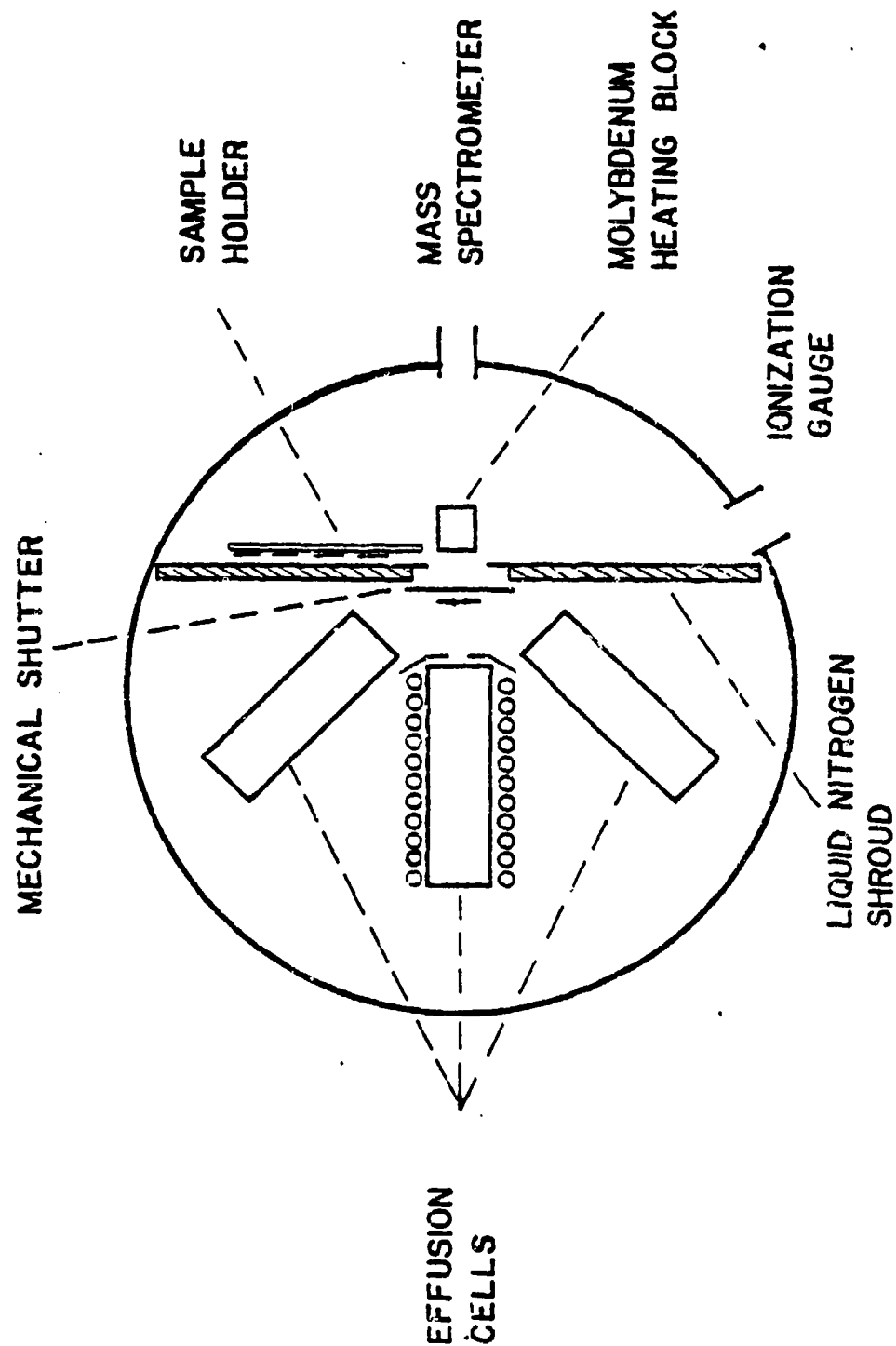


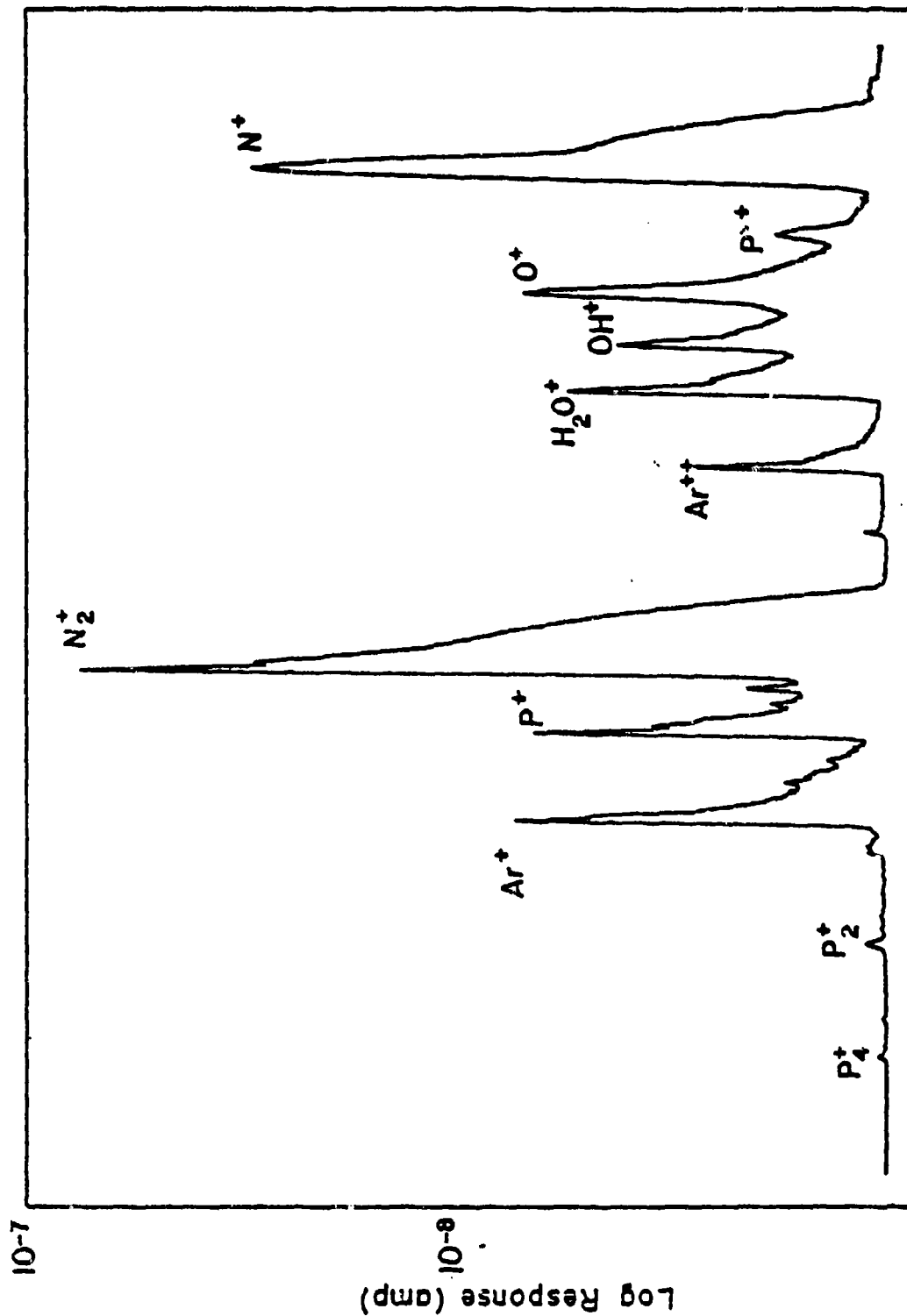
Fig. 13 Diagram of the MBE System

surface of the InP substrates "sees" only the flux from the effusion cells surrounded by a 77°K background.

The vacuum is maintained by a 500 liter/sec ion pump, the liquid-nitrogen-cooled shield, and a back-up titanium sublimation pump. Although at the present time no extensive vacuum system bake-out is performed prior to growth, background pressures during operation are in the range from 5×10^{-7} to 2×10^{-6} Torr. The only analytical apparatus on the MBE system are an ion gauge to monitor total pressure and a mass spectrograph to determine the residual and constituent gaseous species. A mass spectrum for the residual gases prior to growth is shown in Figure 14. Other than the usual gases observed in such a vacuum system, we find Ar and P. The Ar is observed since it is used to back-fill the system after each run and the P is due to the phosphorus deposited on the walls of the vacuum system in preceding runs.

4.2 GROWTH PROCEDURE

A large number of runs have been performed with Cd source temperatures from 150 to 275°C, Sn source temperatures from 800 to 930°C, and P source temperatures from 140 to 230°C. For the effusion cell apertures and source-to-substrate distances in our MBE system, these temperatures correspond to the constituent fluxes calculated in Figure 15. The InP substrates in this series of runs were maintained at temperatures in the range from 185 to 250°C.



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Fig. 14 Mass Spectrum for Residual Gases

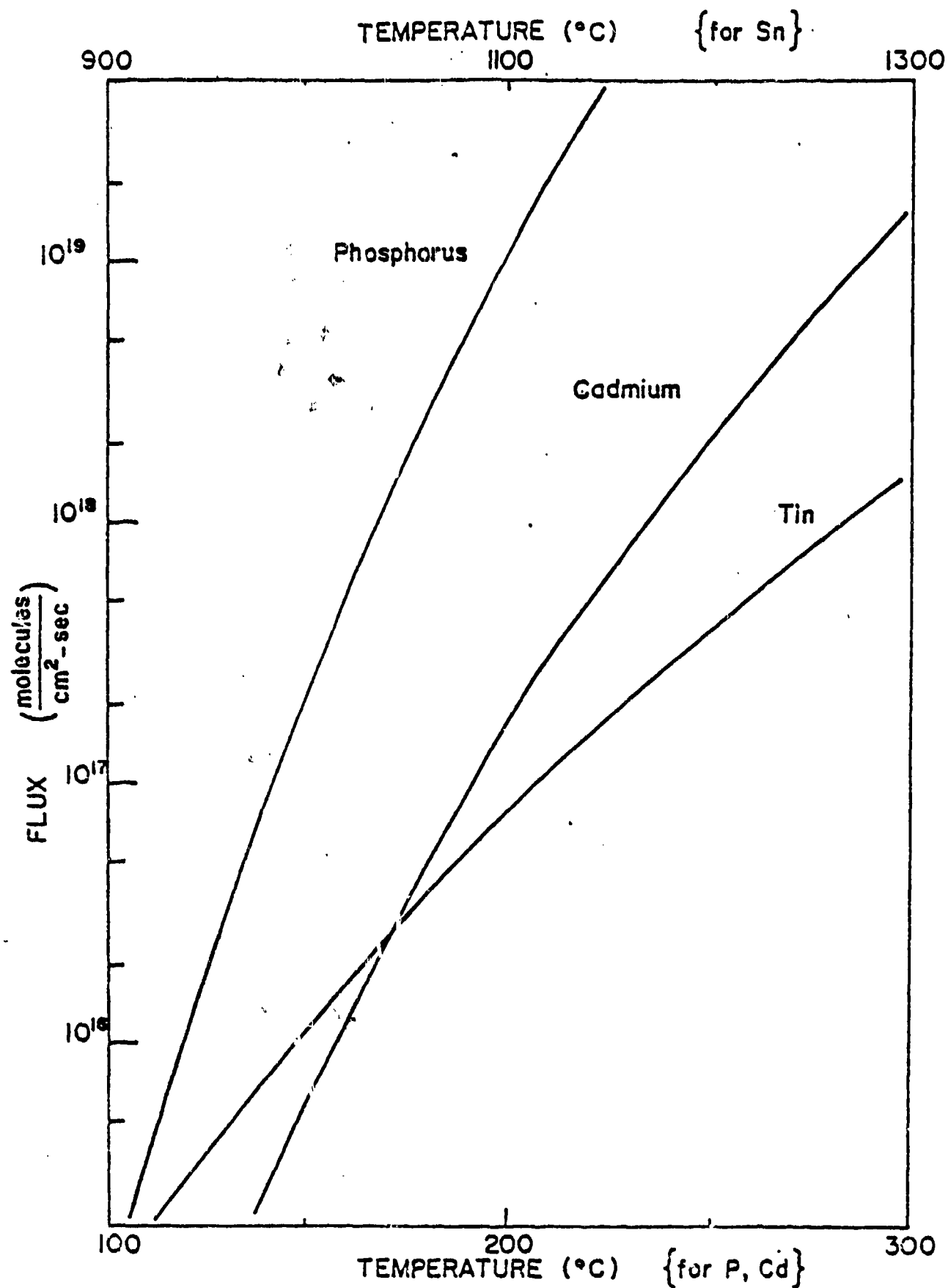


Fig. 15 Calculated Fluxes for Cd, Sn, and P.

4.3 EXPERIMENTAL RESULTS

By heating the InP substrates to the congruent temperature of 365°C ³ prior to the growth process, good quality surfaces have been obtained in this system. During the growth process, however, several problems have been encountered. One is that the evaporation coefficient of phosphorus, defined as the ratio of the apparent vapor pressure in vacuum to the equilibrium vapor pressure, is quite small. We estimate it to be about 10^{-6} which is consistent with previous results⁴. For this reason, the phosphorus furnace has to be maintained at higher temperatures. The tin appears to be reasonably well-behaved with evaporation and sticking coefficients of about 1. The behavior of the phosphorus sticking coefficient is similar to that of arsenic in GaAs MBE or phosphorus in InP MBE⁵: that is, it is on the order of 1 in the presence of a tin beam. The sticking coefficient of cadmium, however, is a problem.

For substrate temperatures above about 200°C in the absence of the other beams, no cadmium deposition has been observed. This is consistent with previous results on the MBE of II-VI compounds⁵. Even with the other beams, however, we have found no cadmium deposition above this substrate temperature over a variety of other conditions. Generally, in the presence of the other beams compositional analyses on the deposited layers have indicated one of the tin-phosphorus compounds: Sn_4P_3 , Sn_3P_4 , or SnP_3 . We have

also attempted to deposit cadmium in the presence of only a tin beam with no success. Apparently, what is happening to the cadmium is very similar to what happens to the volatile constituents in the MBE of III-V or II-VI compounds. That is, the energy of formation of the compound (chemisorption) is required to keep the volatile species from completely desorbing. In the case of cadmium in CdSnP_2 , however, the tin-phosphorus compounds compete with CdSnP_2 over an unknown but substantial range of arrival rates to keep the cadmium from being chemisorbed. For substrate temperatures below 200°C , however, cadmium will stick and we have grown a 1μ thick layer on InP at 185°C which electron microprobe analysis indicates is approximately CdSnP_2 . The layer, however, was polycrystalline with inclusions. Resistivity and Hall measurements gave carrier concentrations and mobilities of $9.5 \times 10^{17} \text{ cm}^{-3}$ and $1150 \text{ cm}^2/\text{V sec}$ at 300°K and $1.0 \times 10^{17} \text{ cm}^{-3}$ and $1400 \text{ cm}^2/\text{V sec}$ at 77°K .

5. DISCUSSION

As indicated above in the MBE system no cadmium deposition was observed for substrate temperatures above 200°C. There are several possible ways to overcome this problem: (1) A cadmium compound (possibly CdP_2) which evaporates in a molecular form could be used as a source. (2) A mechanism could be devised to ionize the cadmium and accelerate it into the substrate region. (3) Extensive deposition rate versus arrival rate data could be compiled with the method used by Smith and Pickhardt⁶ to find a range of arrival rates over which the tin-phosphorus compounds do not compete with CdSnP_2 .

For the polycrystalline growth observed below 200°C, it may be possible to improve the quality of the growth and obtain single-crystal layers by a substantial improvement in the residual pressure of the vacuum system. An alternate approach might be to laser anneal the samples after deposition.

Because of problems with the MBE apparatus we have not been able to pursue any of these potential methods for obtaining single crystal growth of CdSnP_2 . In addition, the results from the open-tube LPE system are more encouraging and we are continuing with the LPE work.

6. REFERENCES

1. E. Buehler, J.H. Wernick, and J.L. Shay, "The CdP₂-Sn System and Some Properties of CdSnP₂ Crystals", *Material Research Bulletin* 6, 303 (1971).
2. J.L. Shay, K.J. Bachman, and E. Buehler, "Preparation and Properties of CdSnP₂/InP Heterojunctions Grown by LPE from Sn Solution", *Journal of Applied Physics*, 45, 1302 (1974).
3. R.F.C. Farrow, *Journal of Physics D* 7, L 121 (1974).
4. J.S. Kane and J.H. Reynolds, *Journal of Chemical Physics* 25, 342 (1956).
5. L.L. Chang and R. Ludeke in "Epitaxial Growth Part A, (Academic Press, New York, 1975) p.37.
6. D.L. Smith and V.Y. Pickhardt, *Journal of Applied Physics* 46, 2366 (1975).